

PATENT ABSTRACTS OF JAPAN

English
Translation

(11)Publication number : 08-174590

(43)Date of publication of application : 09.07.1996

(51)Int.Cl.

B29C 44/00
C08J 9/16
// B29K 67:00
B29K105:04
C08L 67:00

(21)Application number : 06-320627

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(22)Date of filing : 22.12.1994

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(54) THERMOPLASTIC POLYESTER RESIN EXPANDED MATERIAL, THERMOPLASTIC POLYESTER RESIN PRE-EXPANDED PARTICLE AND MANUFACTURE OF THERMOPLASTIC POLYESTER RESIN EXPANDED MATERIAL FROM THE SAME

(57)Abstract:

PURPOSE: To provide manufacture of pre-expanded particles of a thermoplastic polyester resin and manufacture of an expanded material from the pre-expanded particles.

CONSTITUTION: A thermoplastic polyester resin expanded material is prepared by thermally bonding together pre-expanded particles of a thermoplastic polyester resin thereby to form the expanded material, which material has a bulk density of 0.02-0.7g/cm³ and the crystallinity of the expanded material is 15% or more, and the pre-expanded particles are prepared by melting the thermoplastic polyester resin containing a foaming agent by means of an extruder to effect extrusion foaming, following which the extruded foam material is cut, in which the crystallinity of 25% or less is maintained.

LEGAL STATUS

[Date of request for examination] 29.07.1998

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3213871

[Date of registration]

27.07.2001

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The thermoplastic-polyester system resin foaming object characterized by being the foaming object with which the thermoplastic-polyester system resin pre-expansion particle was welded, and the degree of crystallinity of the apparent density gravity 0.02 - 0.7 g/cm³, and a foam being 15% or more.

[Claim 2] The manufacture method of the thermoplastic-polyester system resin pre-expansion particle characterized by making the degree of crystallinity of a pre-expansion particle into 25% or less in the method of fusing, extruding the thermoplastic-polyester system resin containing the foaming agent, foaming to it with an extruder, cutting this extrusion-foaming object subsequently, and manufacturing a pre-expansion particle.

[Claim 3] The manufacture method of the pre-expansion particle according to claim 2 characterized by the melting crystallization temperature of a thermoplastic-polyester system resin constituent being lower than a crystalline melting point 40 degrees C or more.

[Claim 4] The manufacture method of the thermoplastic-polyester system resin foaming object characterized by filling up with a pre-expansion particle the metal mold which cannot be sealed although it can be closed down after fusing the thermoplastic-polyester system resin which contained the foaming agent with the extruder, carrying out extrusion foaming, cutting this extrusion-foaming object subsequently and considering as a pre-expansion particle, carrying out heating expansion of the pre-expansion particle, making a pre-expansion particle comrade weld and considering as a foaming object.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the pre-expansion particle and its manufacture method for manufacturing this foaming object further about the foaming object and its manufacture method of a thermoplastic-polyester system resin (this is hereafter called PAT resin).

[0002]

[Description of the Prior Art] A PAT resin has the outstanding property which is not seen in polystyrene or polyethylene, and rigidity is large, and configuration stability is good, is excellent in chemical resistance etc., and is used in various fields. Therefore, PAT was made to foam like polystyrene or polyethylene and it planned to it is lightweight and make the PAT foaming object excellent in thermal resistance, adiathermancy, buffer nature, etc. the process (sink in) which infiltrates a foaming agent into a resin as one of the methods of making these foaming objects, the process (primary foaming) which heats the resin into which the foaming agent was infiltrated, make foam to it, and make into a pre-expansion particle, and the process (post-expansion fabrication) which fills up metal mold with a pre-expansion particle, make carry out heating expansion, and use as a foaming object pass -- there is a method performed

[0003] However, the PAT resin took the long time for gas barrier - nature to sink in a good hatchet foaming agent, therefore had the trouble of taking time, cost, and time and effort, by this method. For example, the polyester system potential foaming nature moldings into which the low boiling point liquid which is the non-solvent of this polyester or refractory intermediation about high-melting point polyester (PAT resin) at a wet compaction or the non-extended moldings which carried out dry pressing was infiltrated is indicated by JP,51-50365,A, and obtaining a very bulky foam is indicated by by heating this potential foaming nature moldings more than plasticization temperature. However, it supposes that it is so desirable that it is long in order to infiltrate a low boiling point liquid into this poly ester, and making it sink in for 4 to 5 hours or more is indicated. Thus, time great for infiltrating a solvent into polyester is required, and in order to heat at the time of sinking in and pre-expansion particle creation, the degree of crystallinity of a PAT resin rises. Therefore, since the foam of a type object configuration is not obtained in order that a pre-expansion particle comrade may not weld, even if it carries out post-expansion fabrication of the pre-expansion particle of this PAT resin within a mold, filling up this official report with a pre-expansion particle in a mold, and carrying out post-expansion fabrication is not indicated. On the other hand, although the thing of a polypropylene system which is in JP,59-43492,B, and the thing of a polystyrene polyphenylene-ether system which is in JP,4-345635,A are well known as a heat-resistant foaming object, a problem is in use in chemical resistance (oil resistance) or a high temperature region.

[0004]

[Problem(s) to be Solved by the Invention] Emitting into the atmosphere the PAT resin which this invention person made the PAT resin mix a foaming agent using an extruder as a result of examining many things, in order to solve the above-mentioned trouble, and contained the foaming agent, and foaming to it from an extruder Or by being filled up with the foaming particle which was made to cut the extrusion-foaming object before the completion of foaming which was made to complete foaming and was obtained, and after the completion of foaming, and was obtained in a mold, and carrying out post-expansion fabrication It is what the particle comrade found out welding mutually and acquiring a foaming object, and completed this invention. The purpose of this invention obtained [it is filled up with a pre-expansion particle in a mold, carried out post-expansion fabrication, and] and is lightweight. While offering a foaming object with thermal resistance, in order to manufacture the pre-expansion particle for acquiring this foaming object, The manufacture method of a pre-expansion particle of having simplified greatly the process which the process row which infiltrates a foaming agent into a PAT resin is made carrying out heating foaming of foaming agent sinking [PAT] in, and is made into a pre-expansion particle at it, and having excelled in productivity is offered.

[0005]

[Means for Solving the Problem] this invention is the foaming object with which the thermoplastic-polyester

system resin pre-expansion particle was welded, and let the thermoplastic-polyester system resin foaming object characterized by the degree of crystallinity of the apparent density gravity 0.02 - 0.7 g/cm³, and a foam being 15% or more be a summary. This invention is a thing also including the manufacture method of the above thermoplastic-polyester system resin foaming objects. moreover, the method Fuse the thermoplastic-polyester system resin which contained the foaming agent with the extruder, and it emits into the atmosphere from a mouthpiece. It carries out filling up with a pre-expansion particle the metal mold which cannot be sealed although it can be closed down after cutting the extrusion-foaming object before the completion of foaming which was made to complete foaming and was obtained, and after the completion of foaming and considering [or] as a pre-expansion particle, foaming, carrying out heating expansion of the pre-expansion particle, and considering as a foaming object as the feature.

[0006] It may be a single screw extruder, a twin screw extruder, etc. which especially limitation does not have about the extruder used by this invention, and are usually used for extrusion-foaming fabrication of this kind, and you may be the tandem die which connected them further. Various things can be used for the mouthpiece used by this invention. for example, a mouthpiece in a circle and a flat -- a mouthpiece and a nozzle -- a mouthpiece and the multi-nozzle by which further two or more nozzles have been arranged -- metal mold etc. is mentioned Although these mouthpieces can be used and a sheet-like foam, a tabular foam, a rod-like foam, etc. can be made, about the configuration of a foam, you may especially be what configuration.

[0007] In this invention, in order to make an above-mentioned foam into a predetermined configuration, various methods can be used. for example, a mandrel top is gone on when it extrudes from a mouthpiece in a circle -- making -- considering as the shape of a sheet **** -- a flat -- it is made to go on, making it close to the metal plate of a couple, in order to obtain the foam of the tabular which can consider as the shape of a sheet with a chilled roll, and is thick, when extruding from a mouthpiece, and can consider as a predetermined configuration In this invention, an above-mentioned foam is cut and it considers as a pre-expansion particle. It is not limited especially about the method or time of cutting, and various methods can be used. For example, a pelletizer etc. can cut the foam extruded from the nozzle in a predetermined configuration and a size, and let it be a pre-expansion particle, after being let pass and cooled in front of the completion of foaming, or in the tank after the completion of foaming. Moreover, it can extrude from a mouthpiece, can cut immediately before the completion of foaming, or after the completion of foaming, and can also consider as a pre-expansion particle. Moreover, once keeping by the winder etc. what was extruded in the shape of a sheet as the shape of a roll, it is cut by a grinder and the cutter and let it be a pre-expansion particle. As a pre-expansion particle, various things, such as the shape of a pillar, a corniform, and a letter of a chip, can be used, for example.

[0008] In this invention, various methods, such as making air cooling, water cooling, and the cooling system by which the temperature control was carried out contact etc., can be used as the cooling method of a foam. In this invention, it is desirable to perform cooling of a foam as promptly as possible and to make the degree of crystallinity of a pre-expansion particle 25% or less. It is desirable to consider as 15% or less still more preferably [it is desirable and] to 20% or less. If the degree of crystallinity of a pre-expansion particle exceeds 25%, in case heating expansion will be carried out and foaming will be carried out, since weld of pre-expansion particles is bad, the post-expansion force will become weak a foaming object with weak intensity with many openings. Although it is thought that it can be improved by raising the heating temperature at the time of foaming by these, since crystallization of a pre-expansion particle advances further by heating at an elevated temperature, a high molding temperature which a crystal begins to dissolve substantially will be needed.

[0009] In this invention, it is the process which manufactures a pre-expansion particle by extrusion foaming, and in order to stop the degree of crystallinity of a pre-expansion particle low, and in order to improve weld of the pre-expansion particle at the time of post-expansion fabrication, it is desirable to adjust advance of crystallization of a pre-expansion particle. In post-expansion fabrication, in order to carry out heating expansion of the pre-expansion particle with steam etc., crystallization advances simultaneously with a post expansion, and if advance of crystallization is too quick, weld of the post-expansion force or pre-expansion particles will become bad, and will become a foaming object with weak intensity with many openings. The kind of crystalline-nucleus agent, an addition and the molecular weight of a resin, reforming of a resin, etc.

can perform adjusting the speed of crystallization. It is desirable to make it the cold crystallization temperature of a PAT pre-expansion particle become high 40 degrees C or more from a glass transition temperature preferably. Moreover, it is desirable to make it the melting crystallization temperature of a PAT pre-expansion particle become low 40 degrees C or more from a crystalline melting point, and the low still more desirable thing for which 55 degrees C or more are made low is preferably desirable 50 degrees C or more.

[0010] The degree of crystallinity in this invention, a glass transition temperature, cold crystallization temperature, a crystalline melting point, and melting crystallization temperature can use a differential scanning calorimeter (DSC), and can measure it according to JISK-7121. For example, when PAT is used as a polyethylene terephthalate resin, a container is filled up with a measurement sample, a temperature up is performed at the rate of 5 degrees C/min, and the amount of cold heat of crystallization, the amount of heat of fusions and the peak temperature at that time, i.e., cold crystallization temperature, and a crystalline melting point are measured. Cold crystallization temperature is peak temperature to which crystallization takes place at the time of a temperature up, and means that advance of this temperature's crystallization of a low is quick. In this invention, it is desirable to adjust so that 40 degrees C or more of cold crystallization temperature of a PAT pre-expansion particle may become high from a glass transition temperature. Moreover, calculation of degree of crystallinity is calculated by the following formula.

[0011]

[Equation 1]

$$\text{結晶化度\%} = \frac{\text{モル当たりの融解熱量} - \text{モル当たりの冷結晶化熱量}}{\text{完全結晶PAT樹脂のモル当たりの融解熱量}} \times 100$$

[0012] Here, according to the macromolecule data handbook (Baifukan Co., Ltd. issue), since the amount of heat of fusions per mol of perfect-crystal polyethylene terephthalate is set to 26.9KJ, suppose it that this is used. Moreover, measurement of melting crystallization temperature lowers the temperature at the rate of 5 degrees C/min from a melting state, measures the peak temperature of crystallization, and makes it melting crystallization temperature. It means that advance of a crystal is so quick that this melting crystallization temperature is high. In this invention, it is desirable to adjust so that the melting crystallization temperature of a PAT pre-expansion particle may become low 40 degrees C or more from a crystalline melting point, and the low still more desirable thing for which 55 degrees C or more are made low is preferably desirable 50 degrees C or more. The method of filling up with a pre-expansion particle the metal mold which cannot be sealed as a method of fabricating the pre-expansion particle obtained in this invention although it can be closed down, and introducing and fabricating steam as a heating medium further is common.

[0013] Although hot blast, oil, etc. can be used as a heating medium at this time in addition to steam, steam is effective when fabricating efficiently. After fabricating, it is cooled, it is taken out from metal mold and becomes a cast. the case where it fabricates with steam -- a pre-expansion particle -- metal mold -- after being filled up -- first -- low voltage (for example, below 0.5 kg/cm²: wholly gage pressure) -- fixed time steam -- metal mold -- it blows in inside and the air between particles is discharged to the exterior Then, it is the common practice which a pressure up is carried out, and you carry out the post expansion of the pre-expansion particle further, make it weld, and is considered as a cast. As for the degree of crystallinity of the foaming object acquired in this invention, considering as 15% or more is desirable, and it is desirable to consider as 20 more% or more. If degree of crystallinity is lower than 15%, the thermal resistance of a foaming object will fall remarkably.

[0014] Moreover, the density of the foaming object acquired in this invention is 0.02 to 0.7 g/cm³. If smaller [when larger than 0.7 g/cm³, it is inferior to lightweight nature, and] than 0.02 g/cm³, extrusion foaming of pre-expansion particle manufacture is difficult. Preferably, they are 0.06 to 0.5 g/cm³ from 0.04 preferably [cm] 0.06g /to 3 and a pan. In this invention, measurement of the rate of a heating dimensional change is performed as follows. The acquired foaming object was cut into size with an about 10cmx10cmx thickness of 2cm, the rate of change the heat-treatment back of each size (length, width, thickness) and before heating was measured, respectively, and the average of the rate of change of these 3 direction was made into the rate of a

heating dimensional change. Heating conditions were performed at 140 degrees C, and, as for them, two-kind measurement of 1 hour was performed at 180 degrees C for 24 hours. As for the rate of a dimensional change by 140 degree C and 24-hour heating of the acquired foaming object, in this invention, it is desirable that it is less than 5%. Moreover, as for the rate of a dimensional change by 180 degree C and 1-hour heating, it is desirable that it is less than 5%.

[0015] It is chain-like polyester of the amount of macromolecules which dihydric alcohol is made to react to a dicarboxylic acid, and is obtained as a PAT resin used by this invention. As a dicarboxylic acid, although many terephthalic acids are mainly used, it is butylene dicarboxylic-acid, isophthalic-acid, 2, and 6-naphthalene dicarboxylic acid etc. On the other hand, as dihydric alcohol, although ethylene glycol is mainly used, they are a butylene glycol, cyclohexane dimethanol, etc. The things suitable for using by this invention among the above-mentioned PAT resins are polyethylene terephthalate, a polybutylene terephthalate, polyethylenenaphthalate, polycyclohexane terephthalate, etc. Preferably, it is polyethylene terephthalate and a polybutylene terephthalate and is polyethylene terephthalate still more preferably. moreover, an above-mentioned PAT resin is independent -- or it can mix and use An above-mentioned PAT resin can also mix and use other resins for this. When using other resins, it is necessary to make other resins fewer than a PAT resin.

[0016] In this invention, various additives are also mixable. For example, they are a crystalline-nucleus agent, a cellular regulator, a flame retarder, an antistatic agent, a coloring agent, etc. in order [moreover,] to improve the melting property of a PAT resin -- the metallic compounds of acid 2 anhydride like pyromellitic dianhydride, a periodic table Ia like a sodium carbonate, and an IIa group etc. -- a simple substance -- or it can mix and add Although it will be divided [although things various as a foaming agent used by this invention can be used,] into the solid-state compound which decomposes at the temperature more than the softening temperature of a PAT resin, and generates gas, the liquid made PAT resin bashful, the inactive gas which may be dissolved in a PAT resin under pressurization if it divides roughly, and it heats, all can be used in this invention. Solid-state compounds are for example, an AZOII carvone amide, a dinitrosopentamethylenetetramine, a hydra sol KABON amide, a sodium bicarbonate, etc. The liquids to evaporate are a propane, butane, a pentane, saturated aliphatic hydrocarbon like a hexane, benzene, a xylene, an aromatic hydrocarbon like toluene, a methyl chloride, and a halogenated hydrocarbon like Freon (registered trademark). Inactive gases are a carbon dioxide, nitrogen, etc.

[0017]

[Example] An example and the example of comparison are given to below, and the point which is excellent in this invention is explained concretely. The section only means the weight section below.

PET (the Teijin, Ltd. make, TR8580) was used as an example 1PAT resin. First, PET was dried at 160 degrees C for 4 hours, putting PET into a moisture-absorption-and-drying machine, and circulating air of -30 degrees C of dew-points. The following mixture was made using the above-mentioned PET.
PET 100 section pyromellitic dianhydride 0.33 section sodium carbonate the mixture of 0.05 **** -- aperture -- 65mm and ratio of length to diameter -- the extruder of 35 -- putting in -- screw-speed 25rpm and 270 to 290 degree C barrel temperature -- **** -- mixing -- a barrel -- on the way -- as a shell foaming agent -- butane -- pressing fit -- mixture -- receiving -- butane -- 1 % of the weight -- it carried out comparatively extrusion with a mouthpiece in a circle -- a hole -- having -- **** -- extrusion -- slit width was set to 0.4mm and, as for the hole, the bore was set to 60mm extrusion -- PET extruded from the hole foamed, advanced the mandrel top for cooling, carried out mandrel contact, and quenched the inside, and superficies were cooled by blowing air from an air ring Cooling water circulated through the mandrel inside and the front face was held at 20 degrees C.

[0018] What was a cylinder-like was cleared after passing a mandrel, and the foaming PET sheet was rolled round as a flat sheet. For density, 0.20 g/cm³ and thickness were [2.0mm and the width of face of the obtained foaming sheet] 645mm. Moreover, the degree of crystallinity of the foam epidermis section and a core was 10% and 10.5%, respectively. Moreover, 251.5 degrees C and the melting crystallization temperature of the crystalline melting point of the obtained foaming sheet were 195.0 degrees C. After filling up 300mmx400mmx20mm metal mold with it after making the obtained foaming sheet into the abbreviation 5mmx5mmx2mm letter of a chip with a cutter, and sealing it, the vapor pressure made kg [0.3 / /] carry out heating expansion for 120 seconds by 1.0 kg/cm² for 30 seconds by 2 cm. In this way, the PET foaming

object with which an opening is not seen between the particles whose sizes are 300mmx400mmx20mm was acquired. The degree of crystallinity of the acquired foaming object was 23%. the acquired foaming object -- 140-degree C constant temperature -- it was 2.8% when the rate of a dimensional change when putting in into a layer and heating for 24 hours was measured 180 more-degree C constant temperature -- the rate of a heating dimensional change when leaving it in a layer for 1 hour was 3.3% Therefore, it was admitted that the acquired foaming object was excellent in thermal resistance.

[0019] It carried out like the example 1 except having made the addition of pyromellitic dianhydride into the 0.2 weight section in example 2 example 1, using PET (the Teijin, Ltd. make, TR8510) as a PAT resin. For density, 0.2 g/cm³ and thickness were [2.0mm and the width of face of the obtained foaming sheet] 645mm. Moreover, the degree of crystallinity of the foam epidermis section and a core was 8.6% and 9.0%, respectively, and 247.6 degrees C and melting crystallization temperature of the crystalline melting point were 182.1 degrees C. After filling up 300mmx400mmx20mm metal mold with it after making the obtained foaming sheet into the abbreviation 5mmx5mmx2mm letter of a chip with a cutter, and sealing it, the vapor pressure made kg [0.3 / /] carry out heating expansion for 120 seconds by 1.0 kg/cm² for 30 seconds by 2 cm. In this way, the PET foaming object with which an opening is not seen between the particles whose sizes are 300mmx400mmx20mm was acquired. The degree of crystallinity of the acquired foaming object was 21%. the acquired foaming object -- 140-degree C constant temperature -- it was 2.5% when the rate of a dimensional change when putting in into a layer and heating for 24 hours was measured 180 more-degree C constant temperature -- the rate of a heating dimensional change when leaving it in a layer for 1 hour was 3.2% Therefore, it was admitted that the acquired foaming object was excellent in thermal resistance.

[0020] In example 3 example 1, 0.3mm and the bore set slit width of a mouthpiece to 60mm, and trichloromonofluoromethane was performed like the example 1 as a foaming agent except **** for 13 weight sections. For density, 0.06 g/cm³ and thickness were [2.0mm and the width of face of the obtained foaming sheet] 645mm. Moreover, the degree of crystallinity of the foam epidermis section and a core was 10.3%, 10.3%, and 10.5%, respectively, and 251.6 degrees C and melting crystallization temperature of the crystalline melting point were 195.5 degrees C. After filling up 300mmx400mmx20mm metal mold with it after making the obtained foaming sheet into the abbreviation 5mmx5mmx2mm letter of a chip with a cutter, and sealing it, the vapor pressure made kg [0.3 / /] carry out heating expansion for 120 seconds by 1.0 kg/cm² for 30 seconds by 2 cm. In this way, the PET foaming object with which an opening is not seen between the particles whose sizes are 300mmx400mmx20mm was acquired. The degree of crystallinity of the acquired foaming object was 25%. the acquired foaming object -- 140-degree C constant temperature -- it was 4.5% when the rate of a dimensional change when putting in into a layer and heating for 24 hours was measured 180 more-degree C constant temperature -- the rate of a heating dimensional change when leaving it in a layer for 1 hour was 4.8% Therefore, it was admitted that the acquired foaming object was excellent in thermal resistance.

[0021]

[Effect of the Invention] As stated above, in this invention, a foaming agent is infiltrated using an extruder. Therefore, since the thermoplastic-polyester system resin which sank in the foaming agent easily is obtained, extrusion foaming of this is fused and carried out and a pre-expansion object is manufactured Can become 25% or less of degree of crystallinity of a pre-expansion particle, consequently it is filled up with this pre-expansion object in a mold, carry out post-expansion fabrication, and are lightweight. The effect which simplified greatly the process which the process row which a foaming object with thermal resistance can be manufactured [row], and infiltrates a foaming agent into a PAT resin also in the manufacture method of a pre-expansion particle is made to carry out heating foaming of foaming agent sinking [PAT] in, and is made into a pre-expansion particle at it, and was excellent in productivity is done so.